Laboratory Name: National Renewable Energy Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Carbon Nanotube Membranes and Adsorbents

FWP Number: ERWER0L

Program Scope:
Understand the adsorption, transport, and reactivity of molecules such as H_2, CH_4, and CO_2 on the surfaces of carbon nanotube materials and membranes, and on carbon nanotube materials decorated with catalysts. Develop synthetic methods to produce aligned, single crystal arrays of nanotubes. Investigate application of nanotube membranes and materials in gas separation, fuel cell and hydrogen storage applications, and as supports for catalysts.

Major Program Achievements (over duration of support):
Developed, for the first time, rational concept using metal-complexed bucky balls to efficiently store hydrogen reversibly with high gravimetric and volumetric density. Result was co-funded by this program, OS/DMS support of S.B. Zhang (theory), and EERE Hydrogen Program. Chemical vapor deposition growth of carbon single-wall nanotubes (SWNTs) near equilibrium was followed using Raman spectroscopy, permitting the first experimental determination of the Gibbs free energy of SWNT formation. Methane decomposition over alumina supported Fe/Mo catalysts can be controlled to yield predominantly single-walled or double-walled nanotubes. A new synthetic method that combines the best aspects of conventional laser and arc growth methods offers high production rate of low-defect density nanotubes. Platinum-doped nanotubes synthesized by this method show improved activity as fuel cell electrodes. SWNT/polymer composite membranes offer dual transport pathways for improved performance over either material alone. Temperature programmed desorption studies show higher binding energies for CO_2 than for CH_4. Purified, laser-grown carbon single-wall nanotube (SWNT) powders strongly bind CO_2 and only weakly adsorb CH_4 at room temperature and 500 torr. Volumetric measurements show the same result at 200 K, and are in contrast to the literature data for graphite that shows only weak CO_2 adsorption.

Program impact:
Advanced the understanding of hydrogen storage materials. Developed methods to fabricate carbon nanotube membranes. Explored metal-decorated nanotube materials for use in catalysis and fuel cells. Measured the thermodynamics of single-wall carbon nanotube growth. Advanced nanotube growth science and technology.

Interactions:
Internal - OS/DMS Theory (S. Zhang); DOE/EERE/HFCIT program on H_2 storage; OS/DCS Nanoscience "Intermediating Quantum Dot communication with carbon nanotubes and proteins". External - ORNL, LLNL, NIST, NASA, Rochester Institute of Technology, Rice U., U. of Quebec, U. of Michigan, Caltech, Stanford U., U. Pennsylvania, North Carolina State University, Air Products and Chemical, Inc.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Heben - International Energy Agency expert on hydrogen storage; Lead of DOE/EERE Center of Excellence on Carbon-based Hydrogen Storage; Organizer of symposia on Hydrogen Storage Materials at Fall 2004 MRS meeting, Summer 2005 International Partnership for Hydrogen Energy meeting, Spring 2006 MRS meeting, and of symposium on Hydrogen Energy at Spring 2006 ECS meeting. President's Hydrogen Technical Advisory Panel Year 2000 Research Success Story award. Interviewed by Jim Lehrer/PBS News Hour.
Dillon – Organizer Fall 2005 MRS meeting. NSF, MRSEC Review Panels, Women in Science Symposium Series
Dillon/Heben - ~ 22 invited talks since 2001.

Personnel Commitments for FY2002 to Nearest +/- 10%:
M.J. Heben (10%); A.C. Dillon (10%); L. Wagg (100%).

Authorized Budget (BA) for FY02, FY03, FY04:
FY02 BA $252,000 **FY03 BA** $239,000 **FY04 BA** $234,000

Laboratory Name: National Renewable Energy Lab
B&R Code: KC020202

FWP and possible subtask under FWP:
Physics of isoelectronic co-doping

FWP Number:
ERWER2B

Program Scope:

Isoelectronic co-doping GaAs and GaP with Bismuth and Nitrogen is proposed as a novel method for regularizing the abnormal alloy behavior that is observed in these materials when they are doped with Nitrogen alone. The technique will lead to enhancements in 1) the solubility of isoelectronic dopants, and 2) carrier mobilities as compared to doping with Nitrogen alone. The use of the technique will make it possible in several situations to overcome the limitations imposed by semiconductor alloy constraints on the design of some technological important devices such as such as solar cells, lasers and LED's. Most importantly, it will enable the growth of photonic devices on Silicon substrates. The proposed research will advance the basic understanding of the Mott-transition in heavily doped semiconductors as well as help unravel the fundamental mechanisms of alloy formation.

Major Program Achievements (over duration of support):
First observation of Nitrogen resonant level l, of effective mass anomalies, of giant bandgap bowing in GaP, and of the impurity band model. Invention of the concept of isoelectronic co-doping for regularizing optoelectronic properties of GaAs:N and GaP:N. First successful incorporation of Bi into GaAs that showed isoelectronic trap like behavior. The technique of resonant light scattering for probing localized electronic states was pioneered under this project. The research has also led to the first identification of 1) spatially resolved impurity pairs in alloys 2) of giant spin-orbit bowing in semiconductors.

Program impact:
The research resulting from this project has set the trend for most of the current perspective of the mechanisms underlying the giant bandgap bowing in dilute Nitride Alloys. A patent with 135 claims for optoelectronic devices based on the invention of the concept of isoelectrnic co-doping has been awarded and the research has resulted in 40 publications.

Interactions:
Univ. of North Texas, Growth of GaP:N and GaAs:N
Univ. of British Columbia, Growth of GaAs:Bi
Univ. of Montreal, Rutherford Backscattering studies.
Sogang University (Seoul, Korea), LPE growth of GaAs:Bi:N, GaP:Bi:N
Sandia National Labs, Growth of GaAsN Quantum Wells.
National High Magnetic Field Lab., Florida State Univ., High Magnetic Field Studies
Institute of Semiconductors (Beijing), High Pressure studies.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Six Invited Talks, 5 Invited Papers, 40 research publications (1 Phys. Rev Lett.), I patent, 2 book chapt.

Personnel Commitments for FY2002 to Nearest +/- 10%:
Y. Zhang(10%), 1.5 Postdoc, A. Mascarenhas (30%), B. Fluegel (30%)

Authorized Budget (BA) for FY02, FY03, FY04:
FY03 $355K, FY04 $355K, FY05 320K

Laboratory Name: National Renewable Energy Lab
B&R Code: KC020103

FWP and possible subtask under FWP:
Novel Ordered Semiconductor Alloys

FWP Number:
ERWER20

Program Scope:
The research on this project involving ordered semiconductor alloys combines experimental and theoretical efforts aimed at understanding long-range order in isovalent semiconductor alloys. The project includes: (i) MOCVD and MBE growth of III-V alloys such as GaP/InP, GaAs/AlAs (ii) Raman, modulation reflectance, photoluminescence, NSOM, Magneto-PL and reflectance-difference spectroscopy studies of ordering in the above systems, and (iii) first-principles theoretical studies of surface-induced, epitaxially-induced and bulk ordering in various alloys as well as on the electronic bandstructure changes and lattice dynamics changes induced by ordering. The project includes structural studies based on transmission electron diffraction and X-ray scattering for determining the order parameter and involves use of DOE synchrotron facilities.

Major Program Achievements (over duration of support):
Developed the concept of partial ordering, statistical distribution function and order parameter, orientational superlattices, effective mass anisotropy, pyroelectric behavior and spontaneous electric fields. Developed theoretical models for surface induced ordering. First structural and electronic measurements of order parameter. Developed ability to tailor order parameter and consequent electronic properties. Developed the understanding of the lattice dynamics and phonon spectrum of ternary alloy GaInP through control of order parameter. Developed the understanding of the influence of microstructure on the optoelectronic properties of the spontaneously ordered alloy. This work led to the first experimental demonstration of amphoteric (negative and positive) refraction at an orientational domain boundary.

Program impact:
Almost all the present understanding of the electronic properties of spontaneously ordered semiconductor alloys has been pioneered by this program. This understanding is now being exploited for engineering advanced solar cells, HBT transistors for cellular communications, and for novel polarization sensitive optical devices, as well as for providing insights into the exciting phenomenon of negative refraction

Interactions:
University of Houston (S.C. Moss), X-ray and synchrotron studies of order parameter.
Rutgers University (J. Li), Novel Hybrid organic-inorganic superlattices
NHFML-Florida State University, High Field Magneto-PL Studies of Ordered Alloys
Univ. of Erlangen (G. Doehler), Polarization sensitive devices based on ordered alloys.
North Texas University, Ordering in Antimonide Alloys

Recognitions, Honors and Awards (at least partly attributable to support under this FWP):
Our paper on "Amphoteric Refractions" was cited as one of the Top 15 Physics Stories of 2003 as well as cited in Physics Today, 2003. Over 100 Physical Review publications and over 13 Physical Review Letters on the subject of Spontaneous Ordering, Over 24 Invited Talks.

Personnel Commitments for FY2005 to Nearest +/- 10%:
B. Fluegel (35%), Y. Zhang (50%), W. McMahon (50%), Mascarenhas 30% .

Authorized Budget (BA): FY03 $634K, FY04 $634K, FY05 609K

Laboratory Name: National Renewable Energy Laboratory
B&R Code: KC02.0103

FWP and possible subtask under FWP:
Overcoming the doping bottlenecks in semiconductors

FWP Number:
ERWER0K

Program Scope:
The objective of the project is to understand doping limits in various semiconductors and to propose ways to overcome these limits, which is essential to the design of a wide range of new semiconductor devices such as high-efficiency solar cells, blue and UV LEDs and lasers, and detectors with impacts on both nanotechnology and next-generation integrated circuits.

Major Program Achievements (over duration of support):
Developed a theory for equilibrium doping from which one can predict the doping properties of a wide range of semiconductors and alloys. Pioneered the theories for non-equilibrium doping. A number of recent important experimental observations are explained, which include (i) ultrahigh doping of silicon by boron, (ii) p-type conductivity in nitrogen and arsenic doped zinc oxide, (iii) the mysteriously high nitrogen solubility in gallium arsenide, (iv) p-type and bipolarly dopable transparent conducting oxides, (v) theory for n-type diamond, and (vi) defects and doping of quantum dots. Our studies are instrumental to the development of basic understanding of the doping bottlenecks, as well as providing practical recipes to overcome such bottlenecks in wide-gap semiconductors. Band structure engineering by impurities represents another important achievement. The studies of oxygen induced direct-gap, visible light-emitting silicon, band gap tuning by hydrogen in gallium arsenide nitride, and icosahedral symmetry through twinning in silicon nanostructures have added new dimensions to the project.

Program impact:
Fifteen papers were published in Physical Review Letters since FY00. Nature's "Materials Update" had a feature article on Aug. 8, 02 about our proposal of direct-gap, light-emitting silicon. Physical Review Focus reported our work of icosahedral silicon quantum dots on July 2, 04. Overall, our studies provide insights on the microscopic origin of the doping limits in semiconductors, extend the physics of semiconductor point defects into the non-equilibrium growth regime, and suggest new ways to overcome the doping limits, as well as new ways to modify the properties of the host materials. We have been the leader in theoretical study of p-type ZnO and dilute nitrides.

Interactions:
C. G. Van de Walle, Polo Alto Research Center, Inc.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
About 25 invited talks in international conferences since 1999
DOE/BES Chunky Bullet Award, 2002

Personnel Commitments for FY2005 to Nearest +/- 10%:
Shengbai Zhang (Principal Investigator) 5%
Su-Huai Wei (co-PI) 5%
Jinbo Li (post-doc) 50%
Chang-Youn Moon (post-doc) 100%
Ping Zhang (post-doc) 100%
Maohua Du (post-doc) 100%

Authorized Budget (BA) for FY03, FY04, FY05:
FY03 BA $440,000 **FY04 BA** $390,000 **FY05 BA** $374,000

Laboratory Name: National Renewable Energy Laboratory
B&R Code: KC02.0103

FWP and possible subtask under FWP:
Semiconductor Theory

FWP Number:
ERWER62

Program Scope:
A significant part of the U.S. energy-related research is based on semiconductor materials. This project is one of the few basic **theoretical** efforts aimed at providing the fundamental scientific underpinnings for the more empirical experimental investigations in the area of energy-related semiconductors. The semiconductor theory effort addresses a broad base of materials (Si, III-Vs, II-VIs, ternaries) and classes (bulk, defects, surfaces, alloys) and is not restricted to currently operating devices. It is distinct from the EERE-supported projects which focus on applied research on a specifically-defined material system forming the base of current devices. Our effort applies state-of-the-art methodologies of electronic structure theory to address the basic material phenomena required for design of future energy-related devices such as predicting novel compounds, alloy bowing, defect compensation and doping, design of optical materials, surface-induced phenomena, ordering, etc.

Major Program Achievements (over duration of support):
(1) Development of a **Cluster-Expansion** approach for first-principles description of the ground state structures of metal and semiconductor alloys and for predicting their thermodynamic and microstructural properties. (2) Development of the **Inverse Band Structure** approach whereby one identifies the structural configuration having a given target material property (=band gap, effective mass, etc.) (3) Systematic explanation of **basic properties of semiconductor alloys** such as bandgap bowing, phase-separation and ordering, defect compensation, trends in optical properties, phonon instabilities in semiconductors, epitaxial stabilization, clustering and anti-clustering, unusual alloy effects such as giant bowing of nitrogen in III-Vs, ferromagnetism of Mn in III-Vs and II-VIs, and the theoretical basis for spontaneous ordering in semiconductor alloys.

Program impact:
This program has established much of the tools for understanding, analyzing, and design of energy-related semiconductor systems. Over 200 publications, including 80 in *Physical Review Letters* and *Rapid Communications* and over 83 invited talks, including 7 at the American Physical Society (APS) March meeting, have created a broad impact of this work. Many past postdocs from the group occupy academic and National Lab positions (7 were hired by NREL) enhancing the impact of this work. BES projects spun off the present project include "Doping Bottlenecks", "Light Metal Alloys", and "Spontaneous Ordering".

Interactions: N/A

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
(a) To A. Zunger: 39th most cited physicist out of 500,000 physicists surveyed in 1981-1996; American Physical Society **Rahman Award** (2001) for development of first-principles methods; TMS **Bardeen Award** (2001) for theory of spontaneous ordering; 3rd highest cited paper in *Physical Review* since 1893; Five-time invited speaker to APS March meeting; and APS Fellow.
(b) To group Postdocs: 2 APS March meeting invited talks; 23 invited talks at national and international conferences; and placement of past postdocs at numerous faculty and National Lab positions (see http://www.sst.nrel.gov).

Personnel Commitments for FY2005 to Nearest +/- 10%:
A. Zunger, Principal Investigator (10%)
G. Narvaez, Postdoc (100%)
J. Osorio-Guillen, Postdoc (100%)
S. Dudiy, Postdoc (100%)

Authorized Budget (BA) for FY03, FY04, FY05:
FY03 BA $350,000 **FY04 BA** $340,000 **FY05 BA** $350,000

Laboratory Name: National Renewable Energy Laboratory
B&R Code: KC02.0103

FWP and possible subtask under FWP:
Architecture of 3D Million-Atom Nanostructures

FWP Number:
ERWEROP

Program Scope:
Remarkable recent experimental advances in growth, synthesis, as well as in optical and transport characterization of semiconductor nanostructures have created a wealth of unexplained new phenomena and potential applications calling for concomitant theoretical advances. While early experiments have focused on rather small nanostructures ("clusters"), the most modern efforts center on rather large (10^3-10^6 atom) colloidal or "self-assembled" nanostructures, and on **systems** comprising of dots + wires + wells. Until recently, no theoretical methods were available to address atomistically the basic electronic properties (single-body and many-body) of this type of systems. This program started in FY04 has established a novel theoretical technique capable of predicting the optical, electronic, and structural properties of million-atom nanostructure architectures thus enabling the understanding of many of the novel phenomena that have emerged from modern quantum-dot experiments.

Major Program Achievements (over duration of support):
Development of a general method capable of capturing the electronic property of large semiconductor nanostructures and addressing the analysis and design requirements posed by recent experiments. The single-particle properties are calculated via a screened, semi-empirical, pseudopotential approach within the Folded-Spectrum Method, whereas the many-body properties are calculated via configuration-interaction. This approach produces predictions for excitons, (including muti-excitons and charged excitons), Auger recombination, carrier multiplication rates, quantum-entanglement, optical polarization, dot-charging, fine-structure effect, and pressure effect. Recent advances include incorporation of electric field effects, magnetic field effects and piezoelectricity. Applications involve nanostructures of Si, InAs/GaAs, PbSe, CdSe, and higher-level architectures combining dots and wires.

Program impact:
The research resulting from this project created a basis for understanding and analysis of all major optical effects in semiconductor quantum dots.

Interactions:
LBNL: L.-W. Wang, A. Canning
U. of Tennessee: Prof. J. Dongarra
NREL: K. Kim, W. Jones, and P. Graf
Numerous collaborations with experimental groups in the Netherlands, UK, and Germany

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Since the start of this project in 2003, 6 invited talks (two at the APS March meetings) and 21 publications (see http://www.sst.nrel.gov).

Personnel Commitments for FY2005 to Nearest +/- 10%:
A. Zunger, Principal Investigator (10%)
G. Bester, Sr. Scientist (100%)
A.Franceschetti, Sr. Scientist (50%)
J. An, Postdoc (100%)
L. He, Postdoc (100%)

Authorized Budget (BA) for FY03, FY04, FY05:
FY 03 BA $0.0 **FY04 BA $**485,000 **FY05 BA** $450,000